THEORY OF ELECTROLYTIC REDUCTION OF CHROMIC ACID

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THEORY OF ELECTROLYTIC REDUCTION OF CHROMIC ACID

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ABSTRACT. The article reports on the different theories of
electrolytic reduction with respect to use of chromic acid
for industrial electroplating processes. No one theory has
yet been devised which satisfactorily accounts for all
phenomena involved in the electrolytic reduction of chromic
acid. Taking all current theories into consideration, the
author considers it most probable that the process involves
the formation of a film on the cathode with semiconductor
properties which conducts electricity and thereby reduces
the chromic acid.

Electrolysis is the decomposition of electrolytes under the action of   /361*
electric currents. By means of electrolysis, we obtain, today in our indus-
tries, a large number of products. Its importance consists precisely in the
fact that it makes possible production of certain products which cannot be ob-
tained by chemical reactions; or, even if they may be obtained by chemical
reactions, they are still produced by electrolysis because electrolysis yields
a purer product and makes possible a more rational processing of raw materials.

To attain an economical production of a product by electrolysis, i.e., to
achieve a good yield of a product of high purity, the theory of processes
which take place on the electrodes during electrolysis must be known thoroughly.
One of the fields in which electrolysis is used is electroplating. The purpose
of electroplating is to create thin metallic layers by means of electrolysis.
These metallic layers serve for decorative purposes or corrosion protection.
Depending on the function of the electrolytically-produced metallic layer, an
attempt is made to produce a layer of adequate quality. Sometimes the electro-
lytically-produced metallic layer is expected to be shiny, sometimes hard,
sometimes non-porous, at other times, however, it should be porous, etc. Metal
coatings of the same material but of different characteristics can be produced
by electrolysis. However, this is possible only if the theory of electrolytic
precipitation of the appropriate metal is thoroughly known.

Among the electroplating procedures incorporated into everyday practice,
chrome plating is the one most often encountered. In practice, shiny, dull,
whitish, porous, and hard chromium coatings are encountered. It is characteris-
tic that all of them are produced from the same electrolyte, i.e., chromic acid,
and thus it is very important to be acquainted with the theory which provides
the complete picture of how metallic chromium may be precipitated from chromic
acid solutions. Once the theory which regulates a certain technological pro-
cedure is assimilated the procedure may be carried out in exactly the desired
manner.

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*Numbers in the margin indicate pagination in the foreign text.

Unfortunately, because of the very complicated mechanism of chromic acid reduction, no unique theory concerning its reduction on the cathode yet exists; consequently, we present certain existing theories and the results of investigations concerning the electrolytic reduction of chromium acid.

For the electrolysis of a certain electrolyte, an appropriate electrolytic cell is necessary. An electrolytic cell consists of a container and electrodes. The electrode connected to the negative pole of the current source is called the cathode and the other, connected to the positive pole of the current source, is called the anode. During electrolysis, electrochemical reactions occur on the cathode and anode resulting from the participation of not only ions, atoms, or molecules, but also of electrons.

During electrolysis of aqueous solutions of salts, metal or hydrogen are usually obtained as the product on the cathode. Since there are metallic and hydrogen ions already present in the electrolytic solution, the following cathode electrochemical reactions may be written as an example:

$$Cu^{2+} + 2e = Cu$$
$$2H^+ + 2e = H_2,$$
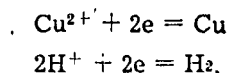
where e represents electrons. The reduction of positive charges in a substance is defined in chemistry as a reduction process, hence, it follows from the above equations that the cupri ions are reduced on the cathode down to metallic copper and the hydrogen ions down to elementary hydrogen. In general, reduction always takes place on the cathode during the electrolysis process.

The cation does not always have to be reduced to metal on the cathode; it may happen that it is only reduced from a higher valence state into a lower one as, for example:

$$Fe^{3+} + 1e = Fe^{2+}$$
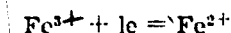
The cathode may also be the location of reduction of certain complex anions such as nitrates, iodates, bromates, chromates, and others whose reduction may be described by the following electrochemical equations:

$$HO_3^- + 4H^+ + 3e = NO + 2H_2O$$
$$IO_3^- + 6H^+ + 6e = I^- + 3H_2O$$
$$CrO_4^{2-} + 8H^+ + 6e = Cr + 4H_2O.$$
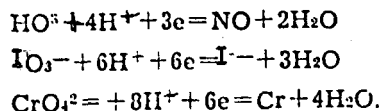
For the ion to react at the electrode, it must be able to reach it. The electric field existing between the cathode and anode directs the motion of the cation towards the cathode and of the anion towards the anode, and thus, to avoid confusion it must be stressed that in the case of anion reduction at the cathode they reach the cathode by means of convection and diffusion, while the diffusion is, in turn, caused by the concentration of anions at the

surface of the cathode. Because of their disappearance this is caused by the cathode reaction.

In contradistinction to the cathode, oxidation is always encountered at the surface of the anode; this may be an anion oxidation such as e.g., oxidation of the chlorine ion down to elementary chlorine, the ferro ion to the ferri ion, or the oxidation of the very metal of which the anode is made; in this case there seems to be a soluble anode. In the majority of electroplating procedures a soluble anode is indeed used so that the composition of the bath during the electrolysis remains unchanged. An exception is encountered in the case of chromium plating where a nonsoluble lead anode made is used on which during the electrolysis, oxygen is developed according to the reductions:

$$4OH = O + 2H_2O + 4e \quad \text{(alkaline medium)}$$
$$4ON = O^2 + 2H_2O + 4e \quad \text{(alkaline medium)}$$
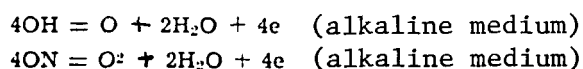
Since we describe in this article a process which occurs at the cathode only, we will not discuss processes connected with the anode.

In a study of the electrolysis of a mixture of electrolytes, the question of which one of them is the first to be decomposed arises. Theoretically, the first electrolyte to be decomposed should be the one requiring the least amount of electrical energy for the process, and since this, in turn, is a product of voltage and amount of charge, it is clear that the electrolyte for which the decomposition voltage is the least will be decomposed first. The decomposition voltage is a quantity characteristic for each electrolyte-electrode system. For instance, if both electrodes are made of platinum and the electrolyte is a mixture of copper sulfate, sulfuric acid, and nickel sulfate, it is found that as voltage gradually increases that the first to decompose on the electrode will be the copper sulfate, then the sulfuric acid, and finally the nickel sulfate. The decomposition voltage may be determined by means of a comparatively simple experiment. For each applied electrode voltage it is only necessary to determine the current and plot a graph such as the one shown in Figure 1. As long as the decomposition voltage is not reached within the cell, there will be for all practical purposes no electrolytic current, i.e., there will exist only a weak current caused by the decomposition of electrolytic impurities whose decomposition voltage is lower than the decomposition voltage of the electrolyte under investigation. Consequently, the voltage which corresponds to point A on the current-voltage curve, as the current OAB is called, represents the decomposition voltages of the electrolyte under consideration. The current-voltage curve obtained in this manner is the result of the processes which take place at the anode and cathode.

The processes which take place during electrolysis may be better understood if the phenomena connected with the cathode or the anode are studied separately. Events which occur at one of the electrodes may be investigated by means of current-voltage diagrams of the electrode which may be registered if either the cathode or the anode, by means of special techniques, is coupled to a certain standard electrode whose electromotive force may be determined by potentiometric means. From the measured electromotive force and the known potential of
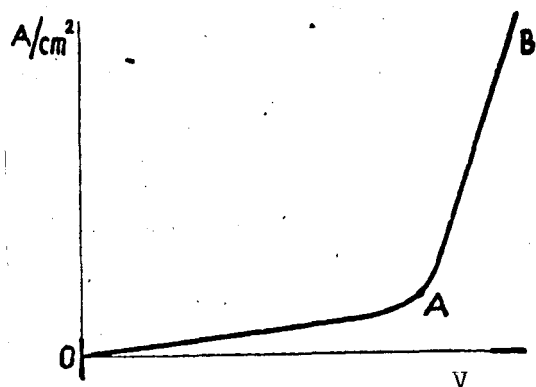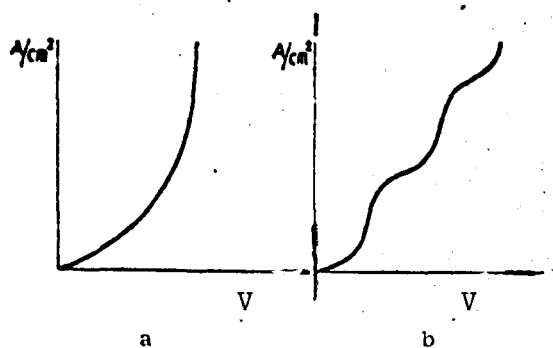
Figure 1.

a   b

Figure 2.

the standard electrode, the potential of either the anode or the cathode may be calculated. Since the cathode or the anode potential may be determined for different current densities in order to avoid the influence of the size of the electrode surface, the cathode or anode potentials are shown graphically as functions of current density. Since during the electrode potential determinations the potential drop between the electrodes caused by the ohmic resistance of the electrolyte are not taken into consideration, electrode potential-current density curves are of much greater importance than the curves determining the decomposition voltage. They are used for the study of the mechanism of reactions taking place at the electrodes.

The electrode for which there exists an equilibrium potential for the given system is dynamically equilibrated with respect to the reactions which take place on it. Thus, for instance, in the case of a copper electrode in the copper sulfate solution there is dynamic equilibrium correspondence between

Cu and $Cu^{++} + 2e$. If it is required to /363

have the reaction $Cu^{++} + 2e$ Cu_3 proceed at the copper electrode at a certain definite rate, a voltage which is more negative than the equilibrium value must be applied to the electrode. This difference between the electrode potential at which a certain reaction takes place on the electrode and the equilibrium potential for the given system represents the polarization value of the electrode. The electrode potential-current density curves indicate precisely the electrode polarization and are called polarization curves.

Polarization curves may have the form shown in Figures 2a and 2b. The horizontal segments on the curve in Figure 2b are caused by some kind of polarization. It will be shown below that this is exactly the case during the reduction of chromic acid on the cathode.

Since during chromium plating, not only chromium but also hydrogen is found liberated at the cathode, a specific feature related to the liberation

of hydrogen at the cathode following the $2H^+ + 2e = H_2$ reaction should be

considered. In aqueous electrolyte solutions hydrogen is not liberated at the equilibrium potential but it is accompanied by a specific polarization

value termed prevoltage which depends on the nature of the cathode, electrolyte, temperature, and current density of the cathode. A substantially more negative potential value than the one for the equilibrium of the given system must be applied to the cathode before liberation of hydrogen can occur. While the prevoltage value of hydrogen on platinum and noble metals is low, it becomes high in the case of such metals as zinc, lead, mercury, and aluminum, and in the case of low current densities it is between 0.6 and 0.8 V. With an increase in current it rises. In the case of chromium the hydrogen prevoltage is not very large and thus it becomes liberated on the cathode during chromium plating.

Having presented some general concepts concerning the reduction on cathodes, we now present the theories pertaining to electrolytic reduction of chromic acid.

In the first place, it may be asked, why electrolytes on the basis of chromo (Cr^{2+}) or chromi (Cr^{3+}) ions are not used in the production of chromium coatings.

The chromo salt solutions are unstable since they oxidize in contact with atmospheric oxygen and the same would happen if they were to come into contact with the oxygen developed at the anode, which means that the cell would have to be equipped with a diaphragm and be hermetically sealed. The use of airtight electroplating cells would not be economical. Attempts to establish good quality chromium coatings from chromo or chromi salts has not yet produced satisfactory results. Consequently, Sargent and Liebereich found simultaneously that good chromium coatings and good utilization of current can be obtained from a solution of chromic acid with an addition of sulfuric acid when the ratio of C_rO_3 to H_2SO_4 = 100:(0.8 to 1.2). This breakthrough was followed by an intensive study on the part of various authors of the electrolytic reduction of chromic acid under different conditions with the aim of establishing a theory of this reduction.

To the present day there does not exist a single accepted theory of electrolytic reduction of chromic acid.

The results achieved in this field are often contradictory as a result of different registration methods; at the onset of these investigations no one know that the presence of certain foreign ions has a great effect on the reduction of chromic acid. Consequently, because of the presence of various impurities, chromic acids of differing origin yielded different results. The greatest number of investigations dealt with the determination of polarization curves for the cathode using the method described briefly below, while the newer methods, which were established after a long suspension in the field of these investigations, are based on the electroplating method. Since a definite theory of chromic acid reduction does not exist, we will present individual theories on the electrolytic reduction of chromic acid as well as the results of certain investigations in this field.

The oldest theory on the reduction of chromic acid is that of Liebreich.

In his investigations Liebreich used platinum and other noble metals for the cathode. Studies were based on determinations of the curved cathode

potential-current density diagram. He came to the conclusion that a cathode-potential-current density curve is not continuous in the case of the chromic acid reduction as shown in Figure 2a but has a discontinuous shape as in Figure 2b, i.e., it consists of several branches. On the basis of such a curve shape as is presented in Figure 3, he came to the conclusion that the chromic acid reduction on the cathode proceeds in stages. Liebreich noted in Figure 3 that along the lowest horizontal branch of the curve he could not observe any changes within the electrolyte around the cathode, nor on the cathode. In the segment of the curve between the points 1 and 2, a change in the color of the electrolyte is observed in the vicinity of the cathode; the solution becomes dark, and it is noted that the dark layer starts to mix with the light layer of the electrolyte. He explained this phenomenon as due to the appearance of chromi ions yielding green. Along this portion of the curve liberation of hydrogen is not observed. A dark red film may be noted at the cathode. The horizontal portion of the curve between the points 2 and 3 corresponds to weak liberation of hydrogen as well as a weak continuation of production of results of chromic acid reduction. Beyond point 3 a liberation of hydrogen and precipitation of metallic chromium are observed. According to Liebreich, the reduction of chromium acid proceeds in following stages:

$$\text{I. } Cr^{6+} + 3e \longrightarrow Cr^{3+}$$

$$\text{II. } 2CrO_3 + 6H^+ + 6e \longrightarrow Cr_2O_3 + 3H_2O$$

$$\text{III. } Cr_2O_3 + 2H^+ + 2e \longrightarrow 2CrO + H_2O$$

$$2H^+ + 2e \longrightarrow H_2$$

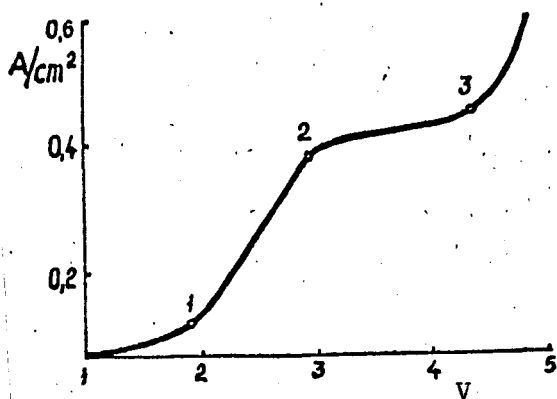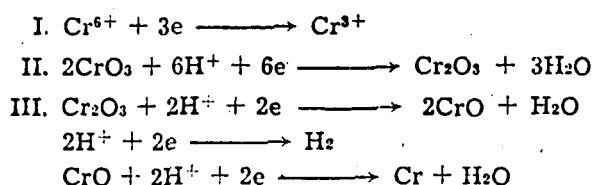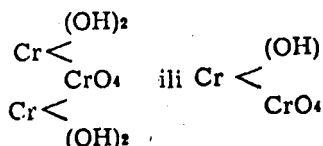$$CrO + 2H^+ + 2e \longrightarrow Cr + H_2O$$

Figure 3

According to this theory, the hexavalent chromium reduces into the trivalent form and between the trivalent chromium and the chromic acid there appear basic chromium chromates forming the cathode film. Since this film is not completely insoluble, it yields trivalent chromium ions which are further reduced to the bivalent form, and this is further reduced to metallic chromium. Since chromium precipitation occurs at a highly negative potential, this is followed by a simultaneous liberation of hydrogen.

Mueller et al, carried out a series of works in order to obtain a theory of chromic acid reduction on the cathode, and this theory is now known as Mueller's theory. If pure chromic acid is subjected to electrolysis precipitation of chromium on the cathode is not observed since, according to Mueller, the cathode becomes covered with insoluble basic chromi-chromate which, though porous, prevents the large chromate ions from reaching the cathode. If metallic chromium is to be obtained on the cathode by electrolysis of chromic acid, the solution must contain some foreign ions such as sulfates, chlorides, fluorides, and certain other anions. Muller concluded that a visible yellow film is not obtained on the cathodes, but that a diaphragm (apourous) film of basic chromates is

created at a potential of + 0.3 V, that this diaphragm changes its appearance at a potential of - 0.7 V, and that it disappears at the potential at which chromium starts to precipitate. This theory explains the appearance of the cathode diaphragm by the initial reduction of chromic acid to the trivalent chromium according to the reaction:

$$HCrO_4^- + 3H_2O + 4e \longrightarrow Cr^{+++} + 7OH^-.$$

This formula indicates that on the cathode surface the solution becomes alkaline and basic chromates are produced at the expense of the trivalent chromi ion and the anion of chromic acid whose composition may be shown by formulas:

$$Cr \Big\langle {\overset{(OH)_2}{\underset{CrO_4}{}}}\quad Cr \Big\langle {\overset{(OH)}{\underset{CrO_4}{}}}$$

$$Cr \Big\langle {\underset{(OH)_2}{}} \quad ili$$

According to Mueller's theory, the molecules of the basic chromi-chromates forming the porous film or cathode diaphragm adhere to the cathode because of cataphoresis and form a layer of oriented molecules where the base part of the molecule is oriented towards the cathode and the acid towards the electrolyte. This is why this diaphragm does not dissolve, since the small pores do not permit access into the diaphragm of chromic acid anions which have a relatively large diameter; if these could reach the base layer of the diaphragm they could make it dissolve. The insolubility of the basic chromi-chromate diaphragm consisting of oriented molecules is used by Mueller as an explanation for the absence of chromium precipitation on the cathode.

A different situation is encountered when some comparatively small anions are present in the solution, such as sulfate and fluoride ions. During cathode polarization, as stated above, a potential is reached when the reduction of chromate down to the chromi ions begins and when the porous cathode diaphragm made of basic chromi-chromate appears. During further polarization of the cathode the small-diameter hydrogen ions penetrate through the pores of the diaphragm towards the cathodes being pulled in this direction by the electric field. In view of the large attractive force between the ions and, since it is impossible to separate the positively charged ions from the negatively charged ions, the hydrogen ions now located within the pores of the diaphragm attract the anions. The higher the cathode polarization the larger the attraction between the cathode and the hydrogen ions, and the more they penetrate the diaphragm the greater is the attraction between the hydrogen ions and the anions. Since the action of large electrostatic forces may cause a deformation of the ions, it is quite possible that at high cathode polarization the hydrogen ions carry deformed small-diameter ions into the pores of the diaphragm which cause dissolution of the diaphragm. If, for instance, fluorine ions are present in the electrolyte, the dissolution of the diaphragm may be described by the equation:

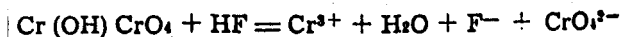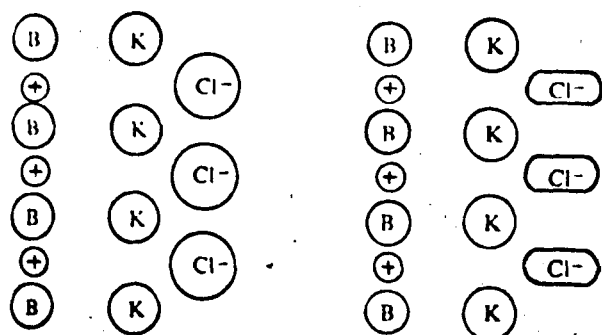$$Cr(OH)CrO_4 + HF = Cr^{3+} + H_2O + F^- + CrO_4^{2-}$$

Figure 4a shows the chemical diaphragm and the position of hydrogen ions and anions for low cathode polarization, and Figure 4b describes the same situation but at high polarization.

a   b

Figure 4

B — basic part of the film
K — acid part
+ — hydrogen ion

The diaphragm behaved in an ideal manner in the case of pure chromic acid, however, it became damaged in the presence of certain small diameter ions which, in turn, allowed access of the chromate ions onto the cathode and their reduction down to metallic chromium.

Mueller was able to prove the existence of the porous cathode diaphragm which was cathode polarized in the chromic acid solution. If treated electrolytic silver from a cyanide solution is deposited on a cathode, it is found that it adheres much less to the support than when it is deposited on a clean metallic surface; this proves the existence of the porous membrane.

Later Mueller came to the conclusion that there exists two types of diaphragms, primary and secondary, since he observed specific influence of the anion on diaphragm disruption depending on the nature of the electrode. Namely, Mueller's results obtained on carbon and platinum cathodes were different.

Weiner carried out extensive investigations of chromic acid reduction on different cathodes. In contradistinction to Liebreich and Mueller, he carried investigations on soluble metals. His experiments showed that gold cannot be viewed as an insoluble electrode and that even platinum during cathode polarization may be activated and made soluble. It is well known that cathode polarization may cause a passive metal to become active, i.e., a soluble electrode. This was also confirmed by electroplating experiments. According to Weiner, cathode potential-current density curves obtained by means of soluble electrodes consist of two branches separated by the limiting current, i.e., they have the shape of the curve in Figure 2b. The curves proper are quite steep. For certain metals such curves are shown in Figure 5 where the horizontal portions connecting the individual branches have been omitted. The last part of the curve, which is the same for all metals, represents the branch corresponding to hydrogen and chromium liberation.

This figure shows that metals which yield two types of ions have two associated branches on the current density-potential curves. On the basis of these results, Weiner concludes that potentials corresponding to cathodes are not caused by the various oxidation stages of chromium since in such a case they would have to be identical for all types of cathodes. These potentials correspond to reversible metal-metallic ion potentials and the oxidation-reduction potentials of the higher and lower valent metallic cation. On this
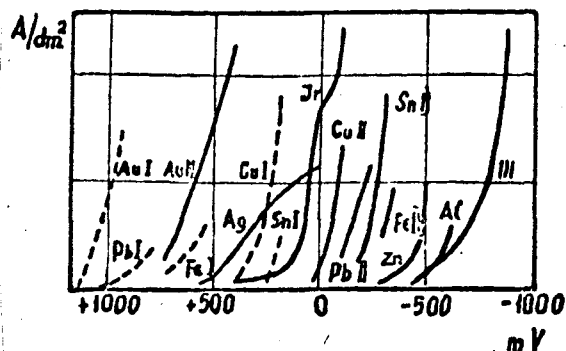
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Figure 5

basis, Liebriech's conclusions seem to be incorrect. Weiner's viewpoint may also be substantiated by the fact that the order in which the branches of the curve are found agree with the electrochemical or Volta sequence, i.e., the sequence is: Au, Ag, Ni, Cu, Pb, Sn, Fe, Zn, and Al. The only exception is Ni but its position near the noble metals may be easily understood in view of its easy passivization.

According to Weiner, the diaphragm at the electrode is fully formed at the end of the second branch of the curve when the potential becomes rapidly more negative and starts materializing the third branch which corresponds to the chromium and hydrogen liberation.

While Mueller attempted to ascribe the importance of the diaphragm during the chromic acid reduction to the oriented molecules of chromi-chromate on the electrode surface, i.e., to assume that this is the reason it is insoluble in chromic acid, Weiner advanced another opinion since he proved on the basis of his investigation that the dissolution rate of basic chromi-chromates in pure chromic acid is very small, and thus that its insolubility need not be explained by a special structure of the layer. In chromic acid containing sulfates, chlorides, or fluorides, the basic chromi-chromates become dissolved and thus diaphragms cannot be formed with low but only with higher current densities.

A more recent work on chromic acid reduction at the cathode by Reinekowski /366 and Knorr shows that the potential-current density curve consists of several branches as was found in earlier results using different methodology. These authors were able to show that even on platinum curves may be obtained which are similar to those obtained on other metals serving as cathodes, which indicates that during cathode polarization and under specified conditions even platinum becomes a soluble electrode. The theory proposed by these authors claims that the individual branches on the current-potential curve correspond to various intermediate products appearing during the reduction and becoming chemisorbed on the surface of the cathode, and these, by their oxidation stage, determine the cathode potential. This new theory seems to agree with Liebreich's and Mueller's theories but not with Weiner's viewpoint.

On the basis of these investigations one may even ascribe a semiconductor property to the diaphragm formed at a cathode during chromic acid reduction which permits the reduction of the cation at the cathode even in the presence of a diaphragm. However, this was already pointed out by Weiner.

In spite of the several theories presented, the question of whether the chromic acid is reduced directly down to the metallic state on the cathode or whether the reduction proceeds by means of intermediate stages still remains unsolved. Even in this respect different viewpoints exist, though recent investigations using radioactive chromium indicate the probability that reduction occurs

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directly from the hexavalent chromium to the metallic state.

Before summarizing the result let us briefly survey the properties of the film or diaphragm which, according to all theories, appears at the cathode during the reduction of chromic acid. According to Liebreich, Mueller, and Weiner there appears at the cathode a film of specific thickness consisting of solid substances which can be proved even by microscopic means. It should be emphasized that these authors do not agree on which branch of the current density-potential curve this film appears. On the other hand, Gerischer and Kappel claim that the film appears on the cathode regardless of the presence or absence of foreign impurity anions within the chromic acid, and this takes place whenever the cathode potential is below + 1100 millivolts; here the film is very thin and its thickness is equal to the size of two layers of molecules. The difference concerning these conclusions originates from the fact that the film thickness measurements utilize different methods. According to the new theory, the cathode film need not be porous to permit a contact between the ions and electrode if it indeed has semiconductor properties. Earlier we presented opinions of certain authors concerning the effects of foreign anions on the diaphragm created at the cathode during chrome plating. According to Gerischer and Kappel, these anions prevent the formation of a secondary thick film which develops in pure chromic acid. One may assume that this secondary film becomes mechanically disrupted by the hydrogen liberated at the cathode.

The existence of the film at the cathode surface gives rise to a very negative potential of chromic acid reduction which is even more negative than the one corresponding to hydrogen liberation and this causes the hydrogen to be liberated simultaneously with chromium. If it is known that at the cathode reduction down to the Cr^{3+} ion also takes place, it becomes clear why the current utilization during chromium precipitation is so low, i.e., about 15%. It is well known that metal precipitation at high polarization leads to a fine small-grain and shiny deposit. This is the reason why chromium was the first metal which in electroplating yielded brilliant shiny coatings. Later this phenomenon was also utilized for the production of other shiny metal coatings.

On the basis of the above, it may be concluded that the theory of electrolytical reduction of chromium is not yet fully developed. For the time being, it may be claimed that a film is created which probably has the properties of a semiconductor and thus permits the passage of electricity and the reduction of chromic acid. An addition of foreign anions augments catalytically the power of chromic acid with respect to the dissolution of basic chromic chromates and for this reason it is difficult to accept Mueller's theory. Of great importance is the behavior of cathodes made of different metals since these influence the potentials of the cathodes as can be seen from Figure 5. Because of a very complicated mechanism the reduction of chromic acid is accompanied by strong polarization and this makes possible the production of brilliant chromium coatings.

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